Notes

Some Rhodium(III)–Dihalogenophosphine Complexes

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Reaction between *trans*-[RhBr(CO)(PEt$_3$)$_2$] and PF$_2$Br at 190 K gives [RhBr(CO)(PEt$_3$)$_2$(P′F$_2$Br)] (1); this rearranges at 215 K to [RhBr$_2$(CO)(PEt$_3$)$_2$(P′F$_2$)] (2). In the analogous iodide system the only product detected was of type (2). Reaction between PF$_2$Cl and [Rh(CO)Cl(PEt$_3$)$_2$] at 190 K gave [Rh(CO)Cl(PEt$_3$)$_2$(P′F$_2$Cl)]; at room temperature the main initial products were PF$_3$ and [Rh(CO)Cl$_2$(PEt$_3$)$_2$(P′FCl)] (3), and on prolonged standing (3) was converted into [Rh(CO)Cl$_2$(PEt$_3$)$_2$(P′Cl$_2$)] (4), also prepared from [Rh(CO)Cl(PEt$_3$)$_2$] and PCl$_3$. Reaction between [Ir(CO)Cl(PEt$_3$)$_2$] and an excess of PF$_2$Cl over a prolonged period at room temperature gave iridium analogues of first (3) and then (4). Reaction between compound (4) and [Ir(CO)Cl(PEt$_3$)$_2$] gave the iridium analogue of (4) and [Rh(CO)Cl(PEt$_3$)$_2$].

In recent papers [1–3] the synthesis of complexes of Ir^{III} containing PF$_2$ or PCl$_2$ groups bound to the metal by reaction between complexes of four-co-ordinated Ir^I and PCl$_3$ or PF$_2$X (X = Cl, Br, or I) has been described. As part of a general study of complexes of this type, we here report the reactions of rhodium(I) complexes with the same halides of P^{III}.

Results

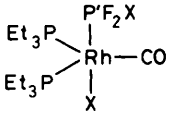
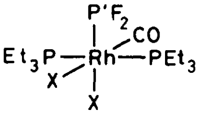
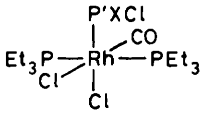
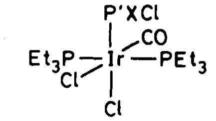
Reaction between [RhBr(CO)(PEt$_3$)$_2$] *and* PF$_2$Br.—The ^{31}P-{^{1}H} n.m.r. spectrum of a solution in toluene of equimolar amounts of [RhBr(CO)(PEt$_3$)$_2$] and PF$_2$Br at 190 K showed that a complex of five-co-ordinated Rh^I containing a PF$_2$Br ligand and formulated as [RhBr(CO)(PEt$_3$)$_2$(P′F$_2$Br)], (1), had been formed. The resonance due to P′, easily identified by the large triplet coupling due to ^1J(P′F), was to low frequency of the value for PF$_2$Br: each line was split into a doublet [^1J(P′Rh) = 226 Hz] of triplets [^2J(PP′) = 63 Hz]; the Et$_3$*P* resonance was in the region associated with Et$_3$P–Rh^I complexes,[4] and appeared as a doublet [^1J(RhP) = 83 Hz] of doublets (63 Hz) of triplets [^3J(PF) = 10 Hz]. At 215 K this complex rearranged irreversibly to give a single complex which was stable up to 275 K. The n.m.r. spectra of the rearranged product lead us to formulate it as the complex of six-co-ordinated Rh^{III}, [RhBr$_2$(CO)(PEt$_3$)$_2$(P′F$_2$)] (2). The resonance due to P′ was at 388 p.p.m., characteristic of M–PF$_2$ complexes; it appeared as a wide triplet [^1J(P′F) = 1 153 Hz] of doublets [^1J(RhP′) = 27 Hz] of triplets [^2J(PP′) = 6.8 Hz]. The resonance due to Et$_3$*P*, this time in the region associated with Et$_3$P–Rh^{III} complexes (δ = 12.6 p.p.m.), was a doublet [^1J(RhP) = 85 Hz] of triplets [^3J(PF) = 15.9 Hz] of doublets [^2J(PP′) = 6.8 Hz]. When the solution was allowed to stand at room temperature the n.m.r. spectrum decayed. The complex was not isolated. The n.m.r. parameters are given in the Table.

Reaction between [Rh(CO)I(PEt$_3$)$_2$] *and* PF$_2$I.—A solution in toluene containing equimolar amounts of [Rh(CO)I(PEt$_3$)$_2$] and PF$_2$I at 190 K gave new peaks in the ^{31}P-{^{1}H} and the ^{19}F n.m.r. spectra corresponding to a derivative of type (2). No resonances that could be assigned to a complex of type (1) were observed. The n.m.r. parameters are given in the Table. The complex was stable in solution up to 275 K, but decomposed on standing at room temperature.

Reaction between [Rh(CO)Cl(PEt$_3$)$_2$] *and* PF$_2$Cl.—At 190 K, a solution in toluene containing equimolar amounts of PF$_2$Cl and [Rh(CO)Cl(PEt$_3$)$_2$] gave n.m.r. spectra which showed that a complex of type (1) had been formed. The only significant difference in the form of the spectra was that ^3J(PF) was not resolved. The n.m.r. parameters are given in the Table. When the solution was allowed to warm to 205 K the lines broadened enough to obscure ^2J(PP′), but the chemical shifts did not change significantly; the broadening of the lines with increasing temperature was reversible. When the temperature was raised above 245 K there were irreversible changes in the spectra. Initially, a weak doublet was observed in the ^{19}F n.m.r. spectrum at −53 p.p.m., in a region associated with M–PF$_2$ species; no corresponding resonance, however, was detected in the ^{31}P-{^{1}H} spectrum. The most abundant species gave P and F resonances that lead us to formulate it as [Rh(CO)Cl$_2$(PEt$_3$)$_2$(P′FCl)], (3). In this complex, P′ is chiral, and so the equivalence of the Et$_3$P groups is destroyed. The spin system P$_A$P$_B$RhP′F is ABMQX. The P′ resonance, at 369.8 p.p.m., showed a doublet [^1J(P′F) = 1 195 Hz] of doublets [^1J(P′Rh) = 26 Hz] of doublets [^2J(PP′) = 3 Hz], emphasizing the non-equivalence of the two Et$_3$*P* nuclei. The Et$_3$*P* resonance was complicated, but could be analysed as the AB part of the spin system, and the derived n.m.r. parameters are given in the Table. If the solution was allowed to warm to room temperature, resonances due to compound (3) grew weaker, and eventually disappeared after 2 h. The ^{31}P-{^{1}H} spectrum at that stage showed resonances associated with a mixture of PF$_3$ and [Rh(CO)Cl(PEt$_3$)$_2$] with peaks due to a fourth complex, [Rh(CO)Cl$_2$(PEt$_3$)$_2$(P′Cl$_2$)] (4), whose synthesis is described below.

Reaction between PCl$_3$ *and* [Rh(CO)Cl(PEt$_3$)$_2$].—A solution in toluene containing equimolar amounts of PCl$_3$ and [Rh(CO)Cl(PEt$_3$)$_2$] at or above 240 K gave a ^{31}P-{^{1}H} spectrum which showed that [Rh(CO)Cl$_2$(PEt$_3$)$_2$(P′Cl$_2$)] had been formed in essentially quantitative yield. The resonance due to P′, at 339 p.p.m., was a triplet [^2J(PP′) = 32 Hz] of doublets [^1J(RhP′) = 24 Hz]. The Et$_3$*P* resonance was a doublet of doublets; the n.m.r. parameters are given in the Table. The complex was isolated and C and H analyses corroborated the proposed formulation. The n.m.r. parameters were the same as those of the ultimate product of the reaction between PF$_2$Cl and [Rh(CO)Cl(PEt$_3$)$_2$].

Table. N.m.r. parameters for some PF_2X, PF_2, PFCl, and PCl_2 complexes of rhodium and iridium

								
Parameter	X = Cl [a]	X = Br [a]	X = Br [b]	X = I [b]	X = F [a,c]	X = Cl [a]	X = F [d]	X = Cl [e]
δ(P′)/p.p.m.	146.0	156.0	388.0	395.4	369.8	339.1	345.2	304.0
δ(P)/p.p.m.	35.0	32.1	12.6	3.4	22.4 17.7	19.2	−6.8 −10.6	−9.2
δ(F)/p.p.m.	−0.1	2.3	−54.7	−52.9	−100.3	—	−101.6	—
$^1J(P'F)$/Hz	1 362	1 362	1 153	1 155	1 195	—	1 121	—
$^1J(P'Rh)$/Hz	250	226	27	25	26	24.2	—	—
$^1J(RhP_A, P_B)$/Hz	74	83	85	86	82 80	79.5	—	—
$^2J(P'P_A, P_B)$/Hz	42	63	6.8	7.3	n.r. 3	32.1	4 31	34.0
$^2J(P_AP_B)$/Hz	—	—	—	—	372.2	—	309	—
$^3J(FP_A, P_B)$/Hz	n.r.	10	15.9	15.4	n.r. n.r.	—	22 n.r.	—

n.r. = Not recorded. Chemical shifts are given as positive to high frequency of CCl_3F (for F), 85% H_3PO_4 (for P). The designation of P_A and P_B is arbitrary: parameters for P_A are given before those for P_B where appropriate.

[a] Recorded in toluene at 190 K. [b] Recorded in toluene at 300 K. [c] From a computer-calculated best fit. [d] Recorded in dichloromethane at 300 K. [e] See ref. 2.

Reaction between $[Ir(CO)Cl(PEt_3)_2]$ *and an Excess of* PF_2Cl.—As described elsewhere,[1] reaction between equimolar amounts of PF_2Cl and $[Ir(CO)Cl(PEt_3)_2]$ at room temperature gives $[Ir(CO)Cl_2(PEt_3)_2(P'F_2)]$, a complex analogous to (2). In the presence of an equimolar excess of PF_2Cl, additional peaks appeared in the ^{31}P-{^1H} and the ^{19}F spectra after the sample had been allowed to stand at room temperature for 2 d. Besides resonances due to PF_3, the additional signals were assigned to $[Ir(CO)Cl_2(PEt_3)_2(P'FCl)]$, analogous to (3). The n.m.r. parameters are given in the Table. After 2 weeks at room temperature, the only resonances were due to PF_3 and to $[Ir(CO)Cl_2(PEt_3)_2(P'Cl_2)]$.

Reaction between $[Rh(CO)Cl_2(PEt_3)_2(P'Cl_2)]$ *and* $[Ir(CO)Cl(PEt_3)_2]$.—The ^{31}P-{^1H} n.m.r. spectrum of a solution in toluene containing equimolar amounts of $[Rh(CO)Cl_2(PEt_3)_2(P'Cl_2)]$ and $[Ir(CO)Cl(PEt_3)_2]$ on warming to room temperature gave the characteristic resonances not of the starting complexes but of $[Rh(CO)Cl(PEt_3)_2]$ and $[Ir(CO)Cl_2(PEt_3)_2(P'Cl_2)]$.

Discussion

Although the chemistry of rhodium is generally analogous to that of iridium, for rhodium the oxidation state III is less stable relative to I. In keeping with this generalization, the reactions between PF_2Br and $[RhBr(CO)(PEt_3)_2]$, and between the corresponding iodides, are very like those in the iridium system, but the resulting rhodium(III) complexes are less stable than their iridium analogues. The consequences of this difference are striking in the reaction between PF_2Cl and $[Rh(CO)Cl(PEt_3)_2]$. The complex of five-co-ordinated Rh^I that is formed at 190 K seems from the broadening of the n.m.r. lines to dissociate fast and reversibly to a small extent between 205 and 240 K before any isomerization to products containing six-co-ordinated rhodium(III) occurs. We were not able to obtain any conclusive evidence for the formation of the expected $[Rh(CO)Cl_2(PEt_3)_2(P'F_2)]$; we suppose that the disproportionation to give first the Rh–P′FCl and finally the Rh–PCl_2 complexes and PF_3 must involve free PF_2Cl, since the analogous disproportionation in the iridium system (which does not dissociate under these conditions) only takes place in the presence of excess of PF_2Cl. The most plausible mechanism involves direct interaction between M–$P'F_2$ and free PF_2Cl, although we cannot exclude a preliminary dissociation; the position of equilibrium favours the formation of hard-substituted PF_3 and softer-substituted M–$P'Cl_2$.

Experimental

Nuclear magnetic resonance spectra were recorded by means of JEOL FX60Q (for P), Varian CFT 20 (for ^{13}C) and XL 100 (for F), and Brucker WH 360 (for P) spectrometers. Volatile compounds were handled using standard vacuum lines fitted with glass taps greased with Apiezon L grease or with grease-free Sovirel rotary valves. Involatile and air-sensitive materials were manipulated using Schlenk methods in conjunction with a Vacuum Atmospheres HE-493 glove-box and Dri-train; microanalysis was performed with a Perkin-Elmer 240 elemental analyser.

Phosphorus trichloride was obtained commercially and purified by distillation on the vacuum line; it was converted into PF_2Br, PF_2I, and PF_2Cl by standard methods.[5] The compound $[Rh(CO)Cl(PEt_3)_2]$ was prepared from $RhCl_3 \cdot 3H_2O$ and converted into the corresponding bromide or iodide by treatment with alkali-metal halides; $[Ir(CO)Cl(PEt_3)_2]$ was prepared[6,7] from $[\{IrCl(C_8H_{14})_2\}_2]$ (C_8H_{14} = cyclooctene), CO, and PEt_3. These complexes were purified by vacuum sublimation.

Reactions in N.M.R. Tubes.—In a typical experiment, $[RhBr(CO)(PEt_3)_2]$ (0.1 mmol) was weighed into an n.m.r. tube; solvent (*ca.* 1 cm^3) was distilled into the tube on the vacuum line, followed by PF_2Br (0.1 mmol). The tube was sealed and kept at 80 K until the n.m.r. spectra of its contents were to be recorded.

Isolation of [Rh(CO)Cl_2(PEt_3)$_2$(P′Cl_2)].—A drop of PCl_3 was added to a solution of [Rh(CO)Cl(PEt_3)$_2$] (0.1 mmol) in degassed toluene. The solvent was pumped away together with excessof PCl_3, the residue was dissolved in the minimum volume of toluene, and the product precipitated by adding light petroleum (b.p. 40—60 °C) (Found: C, 28.7; H, 5.6. $C_{13}H_{30}Cl_4OP_3Rh$ requires C, 28.9; H, 5.6%).

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References

1 E. A. V. Ebsworth, N. T. McManus, D. W. H. Rankin, and J. D. Whitelock, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 244; E. A. V. Ebsworth, R. O. Gould, N. T. McManus, D. W. H. Rankin, M. D. Walkinshaw, and J. D. Whitelock, *J. Organomet. Chem.*, 1983, **249**, 227.

2 E. A. V. Ebsworth, R. O. Gould, N. T. McManus, N. J. Pilkington, and D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.*, 1984, 2561.

3 W. Malisch and R. Alsmann, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 769.

4 T. H. Brown and P. J. Green, *J. Am. Chem. Soc.*, 1970, **92**, 2359; J. S. Al-Sibori, C. Crocker, and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1981, 319; E. A. V. Ebsworth, M. R. Ojeda, and D. W. H. Rankin, *ibid.*, 1982, 1513.

5 J. G. Morse, K. Cohn, R. W. Rudolph, and R. W. Parry, *Inorg. Synth.*, 1967, **10**, 147.

6 T. E. Fraser, Ph.D. Thesis, Edinburgh, 1978.

7 J. Chatt and B. L. Shaw, *J. Chem. Soc. A*, 1966, 1437.

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